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(19) (CA) APPLICATION FOR CANADIAN PATENT (12)

(54) Aqueous Vehicle Composition, Coating Media Containing
This Composition, and Their Use

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Herberts Gesellschaft mit beschränkter Haftung

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Abstract:

An aqueous vehicle composition is described, and also aqueous coating media which can be produced therefrom and their use 10 in the production of multilayer coatings. The vehicle composition contains:

A) 10 ~ 90 weight % of one or more compounds acting as crosslinking agents with an average of at least two 15 acidic CH hydrogen atoms and

B) 10 - 90 weight % of one or more (meth)acrylic copolymers, polyesters or polyurethane resins suitable 20 for the Michael addition, with at least two α,β -unsaturated groups bonded via the carbonyl carbon atom of

25 O O O
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 -C-, -C-O- and/or -C-N-, with a C=C equivalent weight of 85 - 1800 and a number average molecular weight (M_n) of 170 - 10,000 g/mole,

30 wherein the equivalent ratio of A:B is 2:1 to 1:2;

C) 0.01 - 5 weight %, based on the sum of the weights of components A) and B), of a catalyst in the form of a Lewis or Brönsted base, wherein the conjugate acids of 35 the latter have a pKa value of at least 10,

and also water and optionally solvents, pigments, extenders, the usual lacquer auxiliary process materials and/or additives.

2. A vehicle composition according to claim 1, containing a crosslinking component A) with an average of at least two acidic CH hydrogen atoms which originate from one or more of the following groupings, which may be the same or different:
- 5



15 wherein $W_1 = \begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-, -\text{C}-\text{O}-, \end{array} \begin{array}{c} \text{O} \\ \parallel \\ \text{C}-\text{N}-, \end{array} \begin{array}{c} \text{O} \\ \parallel \\ -\text{P}=\text{O}, \end{array} -\text{CN} \text{ or } \text{NO}_2$

20 $W_2 = \begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-, -\text{C}-\text{O}-, \end{array} \begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{N}-, \end{array} \begin{array}{c} \text{O} \\ \parallel \\ -\text{P}=\text{O} \text{ or } -\text{CN}, \end{array}$

25 $W_3 = \begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-, -\text{C}-\text{O}-, \end{array} \begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{N}-, \end{array} -\text{H}, \text{ alkyl or alkyls,}$

30 wherein the $-\text{C}-\text{O}-$ and $-\text{C}-\text{N}-$ radicals are each bonded via the carbon atom on the CH group and the CH group is bonded via at least one of the radicals W_1 , W_2 and/or W_3 to a polymeric or oligomeric unit.

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3. A vehicle composition according to one of claims 1 or 2, characterised in that it exists in aqueous form with a content of organic solvents of 0-20 weight % based on the total coating medium.

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4. An aqueous coating medium containing the vehicle composition according to any one of claims 1 to 3 and in addition one or more organic solvents, and optionally pigments and/or extenders and/or the usual lacquer additives.

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5. A coating medium according to claim 4 as a clear lacquer, covering lacquer, base lacquer or extender.
- 5 6. A process for producing coatings by the application of a coating medium to a substrate to be coated and the subsequent thermal hardening of the coating obtained, characterised in that a coating medium according to one of claims 4 or 5 is applied.
- 10 7. A process for producing multilayer coatings by the application of an aqueous base lacquer to a substrate to be coated, optionally a brief aeration and the wet-in-wet application of a clear lacquer and subsequent joint hardening, characterised in that aqueous coating media according to one of claims 4 or 5 are used as the base lacquer and/or clear lacquer.
- 15 8. The use of the aqueous vehicle composition according to any one of claims 1 to 3 in the production of coatings.
- 20 9. A use according to claim 8 for the production of multilayer coatings.
- 25 10. The use of the aqueous vehicle composition according to any one of claims 1 to 3 for the production of coating media hardenable at temperatures from 5 to 180°C.
- 30 11. The use of the coating medium according to claim 4 or 5 for the production of coatings for motor vehicle series manufacture and repair.

Herberts Gesellschaft mit beschränkter Haftung

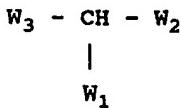
5 An aqueous vehicle composition, coating media containing this
composition, and their use

This invention relates to an aqueous coating medium which is suitable for the production of base-, clear- and covering lacquer coatings, extender layers and primer coats, 10 particularly in the production of multilayer coatings in the motor vehicle industry.

Coating media are known which are based on acidic CH compounds and olefinically unsaturated compounds. For example, EP-A-0 15 224 158 describes two-component lacquers which contain components of this type. These two-component lacquers can be thermally hardened; the hardening reaction is catalysed by Lewis and/or Brönsted bases. Acetoacetate polymers as crosslinking agents for acryloyl-unsaturated acrylates are 20 described in EP-A-0 027 454. Systems of this type are suitable for the production of various coatings. These two-component lacquers still contain appreciable amounts of solvent and therefore possess disadvantages from the point of view of current environmental policies.

25 The object of the present invention is the preparation of a vehicle composition which is suitable for the production of aqueous coating media with a low solvent content and which can be hardened rapidly at low temperatures, e.g. at room 30 temperature, to form films of good hardness and good resistance to water and solvents.

It has been shown that this object can be achieved by means 35 of an aqueous vehicle composition, which forms one subject to which the present invention relates, and which contains:



$$W_2 = -C=O, \quad -C(=O)O-, \quad -C(=O)-N-, \quad -P(=O)(=O)O- \text{ or } -CN,$$

$$W_3 = -C=O, \quad -C(=O)O^-, \quad -C(=O)-N^+, \quad -H, \quad \text{alkyl or alkyls},$$

wherein the alkyl and alkyls preferably have 1 to 6 C atoms
and wherein the carboxyl or carbonamide groups defined above
for the W_1 , W_2 and/or W_3 radicals are each bonded via the
carbon atom to the CH group and the CH group is bonded via at
least one of the W_1 , W_2 and/or W_3 radicals to a polymeric or
oligomeric unit. The acidic CH functionality of component A)
amounts on average to > 2 per molecule. Therefore, when W_3
in the above general formula denotes a hydrogen atom, one
group of this type is sufficient, since it has two acidic
hydrogen atoms.

As mentioned above, the acidic CH functionality of component A) is on average > 2. This means that monofunctional molecules may also be used in admixture with molecules of higher functionality.

40 The acidic CH crosslinking compounds are preferably substantially free from primary, secondary or tertiary amino groups, since these can have a negative effect on storage stability and light-fastness.

hydroxypolyesters with acrylic acid, polyacrylates obtained by the reaction of acrylic acid with vinyl polymers containing epoxide groups, e.g. copolymers of glycidyl (meth)acrylate or vinyl glycidyl ether. The term "(meth)acrylic" is to be understood, both here and below, as representing acrylic and/or methacrylic.

5 Mixtures of the above compounds may also be used as component B).

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The C=C equivalent weight of component B) is 85 to 1800, for example, preferably 180 to 1200, and the number average molecular weight (M_n) is 170 to 10,000, for example; preferably 500 to 5000.

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The vehicle compositions according to the invention may also contain 2-acetoacetoxy-ethyl(meth)acrylate as a reactive diluent for adjusting the viscosity.

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The coating medium according to the invention comprises a mixture of the acidic CH crosslinking component A) and the vehicle B). Mixtures of different components A) or B) may also be used. The vehicles are compatible with each other and may optionally contain solvents to improve their miscibility.

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The preferred solvents for this purpose are those which do not subsequently have a negative effect in the lacquer.

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The ratio of the two components A) and B) depends upon the number of available acidic C-H hydrogen atoms in the crosslinking component and on the number of unsaturated groups of the α,β -unsaturated bond. Since the reactive groups can be determined titrimetrically, accurately adjusted stoichiometric mixture ratios can be achieved. The equivalent ratio of the acidic CH groups to the α,β -unsaturated groups is preferably 0.75:1 to 1.25:1. By this means a sufficient density of crosslinking is generally obtained.

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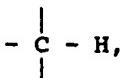
- A) 10 - 90 weight % of one or more compounds acting as crosslinking agents with an average of at least two acidic CH hydrogen atoms and
- 5 B) 10 - 90 weight % of one or more (meth)acrylic copolymers, polyester- and/or polyurethane resins suitable for the Michael addition, with at least two α,β -unsaturated groups bonded via the carbonyl carbon atom of
- 10
$$\begin{array}{c} \text{O} & \text{O} & \text{O} \\ || & || & || \\ -\text{C}- & -\text{C}-\text{O}- & -\text{C}-\text{N}- \end{array}$$
, with a C=C equivalent weight of 85 - 1800 and a number average molecular weight (M_n) of 170 - 10,000 g/mole,
- 15 wherein the equivalent ratio of A:B is 2:1 to 1:2;
- C) 0.01 - 5 weight %, based on the sum of the weights of components A) and B), of a catalyst in the form of a Lewis or Brönsted base, wherein the conjugate acids of the latter have a pKa value of at least 10,
- 20 and also water, and optionally solvents, pigments, extenders, and the usual lacquer auxiliary process materials and/or additives.
- 25 The aqueous vehicle compositions according to the invention can be processed to form aqueous coating media which in addition to the vehicle composition contain one or more organic solvents, and optionally pigments and/or extenders and/or the usual lacquer additives. They may optionally also contain other vehicle components.
- 30 The acidic CH crosslinking agents used as component A) in the coating media according to the invention preferably comprise those which contain at least two acidic CH hydrogen atoms which originate from one or more of the following groupings, which may be the same or different:
- 35

Examples of acidic CH crosslinking components A) which correspond to the above general formula are given below. These examples are subdivided below into three groups: A1, A2, and A3.

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Group A1 contains components with an average of at least two groups with active hydrogen atoms, of the type

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in the molecule, which are derived from methanecarboxylic acid monoamide units or acetoacetic acid ester-2-carboxylic acid amides.

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Examples of suitable A1 compounds comprise reaction products of malonic acid, such as malonic acid dimethyl, diethyl, dibutyl or dipentyl esters, or acetoacetic acid esters, such as acetoacetic acid methyl, ethyl, butyl or pentyl esters, with polyisocyanates.

25

Examples of isocyanates of this type which may be used according to the invention comprise (cyclo)aliphatic or aromatic polyisocyanates such as tetramethylene diisocyanate, hexamethylene diisocyanate, 2,2,4-trimethylene diisocyanate, 1,12-dodecane diisocyanate, cyclohexane 1,3- and 1,4-diisocyanates, 1-isocyanato-3,3,5-trimethyl-5-isocyanato-methylcyclohexane (= isophorone diisocyanate; IPDI), perhydro-2,4'- and/or 4,4'-diphenylmethane diisocyanate, phenylene 1,3- and 1,4-diisocyanates, toluene 2,4- and 2,6-diisocyanates, diphenylmethane 2,4'- and/or 4,4'-diisocyanate, 3,2'- and/or 3,4-diisocyanato-4-methyl-diphenylmethane, naphthalene 1,5-diisocyanate, triphenylmethane 4,4'-triisocyanate, tetramethylxylylene diisocyanate or mixtures of these compounds.

In addition to these simple isocyanates, other isocyanates which contain het roatoms in the radical linking the isocyanate groups are also suitable. Examples of these include carbodimide groups, allophanate groups, isocyanurate groups, urethane groups, acylated urea groups and polyisocyanates containing biuret groups.

The known polyisocyanates which are mainly used in the production of lacquers are particularly suitable for the process according to the invention, e.g. modification products of the above-mentioned simple polyisocyanates which contain biuret, isocyanurate or urethane groups, particularly tris-(6-isocyanatoethyl)-biuret or polyisocyanates containing low molecular weight urethane groups, such as those which can be obtained by the reaction of IPDI present in excess with simple polyhydric alcohols with molecular weights in the range 62-300, particularly trimethylolpropane. Any mixtures of the above-mentioned polyisocyanates may also of course be used for the production of the products according to the invention.

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Other suitable polyisocyanates comprise the known prepolymers containing terminal isocyanate groups, such as those which are obtainable by the reaction of the above-mentioned simple polyisocyanates, primarily diisocyanates, with stoichiometric amounts of organic compounds with at least two groups which are capable of reacting with isocyanate groups. Isocyanates such as these which are preferably used comprise compounds with a total of at least two amino groups and/or hydroxyl groups, and with a number average molecular weight of 300 to 10,000, preferably 400 to 6000. The corresponding polyhydroxyl compounds are preferably used, e.g. the hydroxypolyesters, hydroxpolyethers and/or the acrylic resins containing hydroxyl groups which are known in the art in polyurethane chemistry.

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In these known prepolymers the ratio of isocyanate groups to hydrogen atoms which are reactive towards NCO corresponds to

1.05 to 10:1, preferably 1.1 to 3:1, the hydrogen atoms preferably originating from hydroxyl groups.

In addition, the type and quantitative proportions of the starting materials used in the preparation of the NCO prepolymers are preferably selected so that the NCO prepolymers a) have an average NCO functionality of 2 to 4, preferably of 2 to 3, and b) have a number average molecular weight of 500 - 10,000, preferably of 800 - 4000.

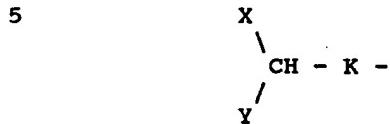
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Reaction products of monoisocyanates with esters and partial esters formed between polyhydric alcohols and malonic acid are also suitable as A1 compounds, however. Examples of polyhydric alcohols include dihydric to pentahydric alcohols such as ethanediol, the various propane-, butane-, pentane- and hexanediols, polyethylene- and polypropylene diols, glycerine, trimethylolethane and -propane, pentaerythritol, hexanetriol and sorbitol. Examples of suitable monoisocyanates include aliphatic isocyanates such as n-butyl isocyanate, octadecyl isocyanate, cycloaliphatic isocyanates such as cyclohexyl isocyanate, aryl-aliphatic isocyanates such as benzyl isocyanate or aromatic isocyanates such as phenyl isocyanate.

Also suitable are the corresponding malonic esters of acrylic resins containing OH groups, polyesters, polyurethanes, polyethers, polyester amides and imides and/or the reaction products of malonic acid half esters such as malonic acid monoethyl ester with aliphatic and aromatic epoxy resins, e.g. acrylate resins containing epoxide groups, glycidyl ethers of polyols such as hexanediol, neopentyl glycol, diphenylolpropane and -methane and hydantoins containing glycidyl groups. Mixtures of these compounds are also suitable.

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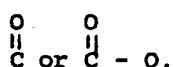
The examples of Group A2 given below comprise a suitable hardener component with active CH groups, which contains at least two groups corresponding to formula (I)



10 or structural units corresponding to formula (I') or (I'')



15 where K represents



20 and where the latter group is bonded via the C atom to the CH group;

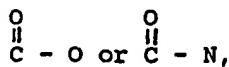
X and Y are the same or different

25 R¹ - C ,
 CO₂R¹, CN, NO₂, CONH₂, CONHR¹H, CONR¹R¹, wherein the R¹ radicals may be the same or different and represent a hydrocarbon radical, preferably an alkyl radical with 1 to 12, 30 most preferably 1 to 6 C atoms, which may also be interrupted by oxygen or an N-alkyl radical, subject to the proviso that only one of the two radicals X, Y may represent an NO₂ group;



wherein the latter group is bonded to the CH group via the C atom;

X', Y' are the same or different



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subject to the proviso that when K' and X' represent



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the Y' radical is not the same as



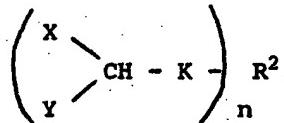
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The number of groups (I) in the hardener according to the invention is preferably 2 to 200, most preferably 2 to 10, the larger numbers relating to oligomeric or polymeric products and representing average values here.

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The hardener components A2 which can be used according to the invention preferably correspond to formula (II)

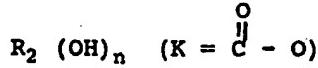
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where X, Y and K have the meanings given above, R² represents a polyol radical

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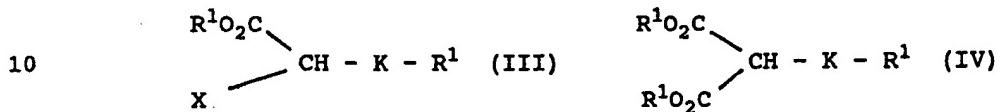
or a polycarboxylic acid radical R²

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and n is at least 2, preferably 2 to 200, most preferably 2 to 10. In the case of oligomeric or polymeric hardener components these numbers are again average values.

- 5 Also preferred are hardener components which fall within Group A2 and which are obtained by the alcoholysis of compounds of formula (III) or formula (IV)



with polyols $\text{R}^2(\text{OH})_n$, where X, K and R^1 have the meanings given above.

- 15
- The above-mentioned polyols $\text{R}^2(\text{OH})_n$ may be polyhydric alcohols which preferably contain 2 to 12, most preferably 2 to 6, carbon atoms. Examples of these include: ethylene glycol, 1,2-, and 1,3-propylene glycol, 1,4- and 2,3-butylene glycol, di- β -hydroxyethyl butanediol, 1,6-hexanediol, 1,8-octanediol, neopentyl glycol, 1,6-cyclohexanediol, 1,4-bis-(hydroxymethyl)-cyclohexane, 2,2-bis-(4-hydroxycyclohexyl)-propane, 2,2-bis-(4- β -hydroxyethoxy)phenylpropane, 2-methyl-1,3-propanediol, glycerine, trimethylolpropane, 1,2,6-hexanetriol, 1,2,4-butanetriol, tris-(β -hydroxyethyl)-isocyanurate, trimethylolethane, pentaerythritol and their hydroxyalkylation products, and also diethylene glycol, triethylene glycol, tetraethylene glycol, polyethylene glycols, dipropylene glycol, tripropylene glycol, polypropylene glycols, dibutylene glycol, polybutylene glycols and xylynene glycol. Moreover, polyesters can be used which are obtained from or using lactones, e.g. ϵ -caprolactones, or hydroxycarboxylic acids, such as hydroxypivalic acid, ω -hydroxydecanoic acid, ω -hydroxycaproic acid or thioglycollic acid, for example. In the case of polyhydric alcohols of this type, the subscript n in the above formula (II) preferably represents 2 to 4.
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- 25
- 30
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Alternatively, the polyol may comprise an oligomeric or polymeric polyol compound (polyol resin), the number average molecular weight of which (determined by gel chromatography using polystyrene as the calibration standard) is usually in the range from about 170 to 10,000, preferably about 500 to about 5000. However, in special cases the molecular weight may be 10,000 and above. The oligomers/polymers comprise polymerides, condensation polymers or addition polymer compounds. Their hydroxyl number is generally 30 to 250, preferably 45 to 200, most preferably 50 to 180 mg KOH/g. These compounds, which contain OH groups, may also optionally contain other functional groups such as carboxyl groups.

Examples of polyols of this type include polyether polyols, polyacetal polyols, polyester amide polyols, polyamide polyols, epoxy resin polyols or their reaction products with CO₂, phenol resin polyols, polyurea polyols, polyurethane polyols, polyols of cellulose esters and ethers, partially saponified homo- or copolymers of vinyl esters, partially acetalated polyvinyl alcohols, polycarbonate polyols, polyester polyols or acrylic resin polyols. Polyether polyols, polyester polyols, acrylic resin polyols and polyurethane polyols are preferred. Polyols of this type, which may also be used in admixture, are described in DE-A-31 24 784, for example.

Examples of polyurethane polyols include those which are formed by the reaction of di- and polyisocyanates with an excess of di- and/or polyols. Examples of suitable isocyanates include hexamethylene diisocyanate, isophorone diisocyanate, toluene diisocyanate and also isocyanates formed from three moles of a diisocyanate such as hexamethylene diisocyanate or isophorone diisocyanate, and biurets produced from the reaction of one mole of a diisocyanate with one mole of water. Suitable polyurea polyols may be obtained in a similar manner by the reaction of di- and polyisocyanates with

equimolar amounts of aminoalcohols, .g. ethanolamine or diethanolamine.

- Examples of polyester polyols include the known
5 polycondensation products of di- or polycarboxylic acids or their anhydrides, such as phthalic anhydride, adipic acid, etc., and polyols such as ethylene glycol, trimethylolpropane, glycerine, etc.
- 10 Suitable polyamide polyols may be obtained in a similar manner to the polyesters, by replacing the polyols at least in part by polyamines such as isophorone diamine, hexamethylene diamine, diethylene triamine, etc.
- 15 Examples of polyacrylate polyols or polyvinyl compounds containing OH groups include the known copolymers obtained from (meth)acrylic acid esters containing hydroxyl groups or vinyl alcohol and other vinyl compounds, such as styrene or (meth)acrylic acid esters, for example.
- 20 The above polycarboxylic acids $R^2(CO_2H)_n$, where n is preferably 2 to 4 here, may be of an aliphatic, cycloaliphatic, aromatic and/or heterocyclic nature, and may optionally be substituted and/or saturated, by halogen atoms
25 for example. Examples of carboxylic acids such as these and their derivatives include: succinic acid, adipic acid, suberic acid, azelaic acid, sebacic acid, phthalic acid, terephthalic acid, isophthalic acid, trimellitic acid, pyromellitic acid, tetrahydrophthalic acid, hexahydrophthalic acid, cyclohexane
30 1,3- and 1,4-dicarboxylic acids, di- and tetrachlorophthalic acids, endomethylene tetrahydrophthalic acid and its hexachloro derivative, glutaric acid, maleic acid, fumaric acid, dimeric and trimeric fatty acids such as oleic acid, optionally in admixture with monomeric fatty acids or cyclic
35 monocarboxylic acids such as benzoic acid, p-tert.-butyl benzoic acid or hexahydrobenzoic acid, and also the reaction

products of the above-mentioned polyols $R^2(OH)_n$ with cyclic carboxylic acid anhydrides.

Depending on the type of the polyol or polycarboxylic acid component, the hardener components A2 which can be used according to the invention comprise more or less viscous liquids, or solids which are substantially soluble at least in the usual lacquer solvents and which preferably contain less than 5 weight %, most preferably less than 1 weight %, of crosslinked constituents. The CH equivalent weight, which is a measure of the amount of groups (I) or structural units (I')/(II'') in (A2), is generally between 100 and 5000, preferably between 200 and 2000, and the number average molecular weight (M_n) is generally 200 to 10,000, preferably 500 to 5000 (determined by gel chromatography using polystyrene as the calibration standard). Methods of preparing compounds such as these are described in more detail in EP-A-0 310 011.

Additional examples of hardener components which can be used according to the invention are those of Type A3, in which the CH grouping is derived from a compound containing a $-CO-CHR^3-$ $CO-$, $NC-CHR^3-CO$, $NC-CH_2-CN$, $=PO-CHR^3-CO-$, $=PO-CHR^3-CN$, $=PO-CHR^3-PO=$ or $-CO-CHR^3-NO_2$ grouping, wherein R^3 is preferably a $C_1 - C_8$ alkyl or H, most preferably hydrogen. β -dioxo compounds are preferred.

The above A3 groupings may be bonded to at least one polyvalent monomeric or polymeric compound. For example, they may be bonded to at least one compound of the group comprising monohydric or polyhydric alcohols, polymers containing OH groups, polyamines and polymercaptans. They are polyvalent with respect to their CH function. They may be prepared, for example, by the esterification of a polyepoxide with a $-CH$ carboxylic acid forming the grouping, e.g. acetoacetic acid. An A3 component with two active H atoms for each epoxide

group is obtained in this manner. Aromatic or aliphatic polyepoxides may be used for this purpose.

Examples of suitable compounds of the A3 type include ketones such as acetylacetone, benzoyl acetone or acetyl dibenzoylmethane; esters of optionally alkyl-substituted acetoacetic acid such as α - and/or γ -methyl acetoacetic acid or of acetone dicarboxylic acid; malonic acid units of malonic acid with ester-like bonds, and their monoalkyl derivatives, either straight-chain or branched, with 1 to 6 C atoms in the alkyl radical, e.g. methyl, ethyl and n-butyl and also phenyl; or esters of cyanoacetic acid with monohydric to hexahydric alcohols with 1 to 10 C atoms. The alkyl-substituted esters, e.g. α -methyl or α,γ -dimethyl acetoacetic ester, have only one active H atom and are therefore preferably used in the form of di- or polyesters of polyhydric alcohols, in order to make a sufficient number of reactive groups available. Examples of suitable alcohols for the esterification of the above acids include methanol, ethanol, butanol, octanol and/or polyhydric alcohols or polyhydroxy compounds, the latter two types being preferred. Further examples of A3 compounds include acetoacetic ester, ethanediol-bis-acetoacetic ester, glycerine-tris-malonic acid ester, trimethylolpropane-tris-acetoacetic ester, partial esters of these acids with polyhydric alcohols, and also the corresponding esters of OH group-containing acrylic resins, polyesters, polyethers, polyester amides and imides, polyhydroxylamines, and also nitriles of these acids inasmuch as these exist, e.g. malonic acid mono- or dinitrile, alkoxy carbonyl methanephosphonic acid and the corresponding bis-methanephosphonic acid esters. The above-mentioned acids may also be bonded in the form of amides to amines, preferably polyamines, which may also comprise oligomers and/or polymers, including amine resins, aliphatic amines being preferred.

If polyamines are used as the starting materials, the A3 compounds can be prepared in the form of amides. For example

the starting material may comprise 1 mole of an alkylene diamine, which is reacted with 2 moles of acetoacetic ester with the formation of a compound which also has four H atoms activated by amide groups.

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Reactive nitro compounds are also suitable as A3 compounds, e.g. nitroacetic acid derivatives such as tri-(nitroacetic acid)-glycerine ester or trimethylolpropane nitroacetic acid ester.

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Examples of A3 compounds which form -CH- type groups include diketene and its monoalkyl substitution products, and also tetrahydrodioxin, which can react with suitable components with the formation of acetoacetic ester or amide groups.

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The hardener components A) may be prepared in the usual solvents. It is advantageous if solvents are used which do not impair the subsequent production of the coating medium.

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It is also advantageous if the content of organic solvents is kept as low as possible. If the hardener component A) contains polar groups, e.g. amide or urethane groupings, it is possible to disperse it easily in water. This may optionally be assisted if the crosslinking components contain ionic groups which can be neutralised, e.g. carboxyl groups, in the oligomer or polymer skeleton. Crosslinking agents with ionic groups such as these may be dispersed in water well. At the same time, the content of organic solvents can be reduced to a low value without significantly increasing the viscosity of the crosslinking agent solution.

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(Meth)acrylic copolymers or polyester- and/or polyurethane resins, which are suitable for the Michael addition and which are as defined above, are used according to the invention as component B). They contain at least two groups capable of participating in the Michael addition, i.e. groups which

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contain double bonds activated by at least one negatively polarising group (Michael acceptor). These comprise α,β -

unsaturated groups which can be incorporated in the chains of the copolymers or resins. They may also preferably be side groups and/or terminal groups. Suitable B) compounds are described in DE-PS-835 809, in US-PS-4,408,018 and in EP-A-5 16 16 79 and EP-A- 22 41 58, for example, to which reference is made here. These are compounds (B) with at least two groups corresponding to the formula



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in which:

15 R^5 represents hydrogen or a hydrocarbon radical, preferably an alkyl radical with 1 to 12, most preferably 1 to 4, C atoms such as a methyl, ethyl, n-propyl, iso-propyl, n-butyl or tert.-butyl group;

20 R^4 denotes entities which are the same or different, representing hydrogen, a hydrocarbon radical, preferably an alkyl radical with 1 to 10, most preferably 1 to 4, C atoms, an ester group $-CO_2R^1$, a $-CN$, $-NO_2$, $-SO_2-$, $-CONHR^1$, $-CONR^1R^1$ or $-COR^1$ group, wherein the R^1 's are the same or different and are as defined above for formula I; and

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Z represents $\begin{array}{c} O \\ || \\ -C- \end{array}$, $\begin{array}{c} O \\ || \\ -C- \end{array} - O$, or $\begin{array}{c} O \\ || \\ -C- \end{array} - N -$,

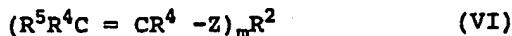
30 wherein the two latter groups are bonded to the CR^4 group via the C atom.

35 R^5 and R^4 in the above $R^5 R^4 - C$ group preferably each represent hydrogen.

The above groups V are indirectly bonded to each other. The indirect linkage concerned may be a hydrocarbon radical, for example, but is preferably the radical of a polyhydric alcohol

or of a polyvalent amine or aminoalcohol. At the same time, this indirect linkage may also be part of the chain of an oligomer and/or polymer, i.e. the group V may exist in the side chains of the oligomers or polymers or may form these
5 side chains.

According to a particular embodiment, the compound B) corresponds to the formula



10 in which R^5 , R^4 and Z have the same meaning as in formula (V), R^2 has the same meaning as in formula (II) and m is at least 2, preferably 2 to 200.

15 The $R^5R^4C = CR^4 - Z$ group - (V) may be derived from a singly or poly-unsaturated mono- or dicarboxylic acid with 2 to 20, preferably 3 to 10, C atoms, for example.

20 Examples of carboxylic acids such as these include crotonic acid and citraconic acid or their anhydrides, sorbic acid, fumaric acid, mesaconic acid, substituted and unsubstituted cinnamic acids, dihydrolevulinic acid, malonic acid mononitrile, α -cyanacrylic acid, alkylidene malonic acid, alkylidene acetoacetic acid, and preferably acrylic acid, methacrylic acid and/or maleic acid or their anhydrides. The
25 linkage of the Michael acceptor to the bonding component which is possible via the group Z or also via the R^4 radical may be effected via ester, amide, urethane or urea groups, as in a polymeric carrier.

30 In accordance with the above, the groups corresponding to formula (V) may be bonded to the radical of a polyol, a polyamine, a polyamide or a polyiminoamide, wherein this radical may also be an oligomer or polymer.

35 The polyols concerned here are basically the same as those listed in detail above in connection with the Michael donor, i.e. polyhydric alcohols or oligomeric or polymeric polyol

compounds, e.g. polyether polyols, polyester polyols, acrylic resin polyols and polyurethane polyols.

The amino group-containing carriers (polyamines) comprise, for
5 example, the above-mentioned alkylene diamines and their oligomers, such as ethylene diamine, propylene diamine, butylene diamine, diethylene triamine, tetramine and higher homologues of these amines, and also amino alcohols such as diethanolamine or the like.

10 Examples of compounds suitable as component B) include: alkyl glycol di(meth)acrylates such as ethylene glycol diacrylate, diethylene glycol diacrylate, propylene glycol diacrylate, trimethylene glycol diacrylate, neopentyl glycol diacrylate,
15 1,3-butylene glycol diacrylate, 1,4-butylene glycol diacrylate, 1,6-hexamethylene glycol diacrylate, 1,10-decamethylene glycol diacrylate, trimethylolpropane triacrylate, pentaerythritol tetraacrylate, pentaerythritol triacrylate and the corresponding methacrylates, and
20 alkoxylated and propoxylated derivatives.

Moreover, the α,β -unsaturated group which is bonded via a carbonyl carbon atom may be bonded to polymers, e.g. condensation polymers such as polyesters or addition polymers such as polyurethanes, polyethers or (meth)acrylic copolymers or vinyl polymers, such as glycidyl (meth)acrylate copolymers. Polymers which should be mentioned here by way of example include urethane acrylates, obtained by the reaction of polyisocyanate such as hexamethylene diisocyanate with hydroxyalkyl acrylates such as hydroxyethyl acrylate, or by the reaction of hydroxyl group-containing polyesters, polyethers or polyacrylates with polyisocyanates and hydroxyalkyl acrylates, urethane acrylates obtained by the reaction of caprolactonediol or -triol with polyisocyanates and hydroxyalkylacrylates, polyether acrylates obtained by the esterification of hydroxypolyethers with acrylic acid, polyester acrylates obtained by the esterification of

The elasticity of the crosslinked product can be controlled within a range of tolerance, e.g. by means of the chain length of the oligomers and/or polymers used for A) and B). The oligomers and/or polymers used may thus be selected according
5 to the desired elasticity of the crosslinked product. The degree of crosslinking can be controlled via the functionality of the compounds A) and B) which are used. Thus the degree of crosslinking can be increased when three or more reactive groups are present in at least one of the compounds A) and B).

10 Component C) consists of catalysts in the form of Lewis bases or Brönsted bases, the conjugate acids of the latter having a pKa value of at least 10. Component C) may consist of one or more catalysts. Examples of Lewis bases which have proved
15 to be particularly suitable include those of the cycloaliphatic amine group such as diazabicyclooctane (DABCO), tert.-aliphatic amines such as triethylamine, tripropylamine, N-methyl diethanolamine, N-methyl diisopropylamine or N-butyl diethanolamine, and amidines such as diazabicycloundecene
20 (DBU) and guanidines such as N,N,N'N'-tetramethyl guanidine. Other examples include alkyl- or aryl-substituted phosphanes such as tributyl phosphane, triphenyl phosphane, tris-p-tolyl phosphane, methyl diphenyl phosphane, and hydroxy- and aminofunctional phosphanes such as tris-hydroxymethylphosphane
25 and tris-dimethylamino ethyl phosphane.

Examples of Brönsted bases which may be used include alcoholates such as sodium or potassium ethanolate, quaternary ammonium compounds such as alkyl-, aryl- or benzyl ammonium
30 hydroxides or halides, such as tetraethyl or tetrabutylammonium hydroxide or fluoride for example, and trialkyl or triaryl phosphonium salts or hydroxides.

35 The amount of catalysts is generally 0.01 to 5 weight %, preferably 0.02 to 2 weight %, based on the total solids content of components A) and B).

The crosslinking component A) and the vehicle component B) or the mixtures thereof are used in aqueous form according to the invention.

5 For this purpose the crosslinking component A) and the vehicle component B) are converted into an aqueous phase, optionally with a low proportion of solvents and optionally together with emulsifying agents. The preferred solvents are those which are miscible with water. The amount of solvent may be up to 10 weight % for example, preferably up to 10 weight %, based on the final aqueous composition. Ionic or non-ionic emulsifying agents, preferably non-ionic emulsifying agents, may be used as the emulsifying agents. The content of emulsifying agent may be 0.5 to 30 weight % for example, 15 preferably between 1.5 and 15 weight %, based on the solids content of component A) and component B) in the final aqueous coating medium.

20 The usual methods familiar to one skilled in the art may be employed for the preparation of the aqueous dispersions. Thus, for example, the solvent-containing forms of components A) and B) or mixtures thereof may be substantially freed from solvents, preferably by distillation under reduced pressure, whereupon the emulsifying agent can be dispersed therein, 25 preferably in the resins or resin mixtures whilst the latter are still warm and of low viscosity. This mixture can then be added to the aqueous phase, with intensive mixing for example. The preparation of the dispersion may also be assisted by heating the aqueous phase. Examples of suitable 30 mixer units include high speed stirrers or rotor/stator mixers. It is also possible to improve the quality of the dispersion by means of high-pressure or ultrasonic homogenisers.

35 Components A) and B) may be mixed first and then emulsified together. However the crosslinking component A) and the

vehicle component B) may of course be emulsified separately and then mixed.

- The process may be carried out continuously or batch-wise.
- 5 The dispersions produced may also be mixed with each other at this time. An aqueous oil-in-water dispersion is obtained which is stable on storage and which can be adjusted with water to give solids contents which are suitable for application. The aqueous dispersions obtained according to
10 the invention may have a solids content in the range of 25 - 55 weight %, for example, based on the final dispersion. They may optionally be diluted with water before their application, e.g. to a viscosity suitable for spraying.
- 15 Commercially available ionic or non-ionic emulsifying agents are suitable as emulsifying agents. For example, the reaction products of alkyl phenols with alkylene oxides may be used, as may the reaction products of sorbitane fatty acid esters with alkylene oxides, e.g. C₁ -C₁₂ alkylphenol ethoxylates.
- 20 As a rule, component C) is water-soluble, but can be emulsified as described if required.

The vehicle compositions according to the invention comprise
25 so-called two-component systems.

Components A) and B) are stored jointly as the vehicle component 1 and component C) is stored as the hardener component 2. If necessary, it is also possible to store
30 component B) as the vehicle component 1 and components A) and C) as the hardener component 2, as long as A) and C) do not react with each other.

This means that components 1 and 2 are stored separately and
35 are only mixed before or on their use, for the production of coating media, for example.

The coating media according to the invention may be produced by the usual methods familiar to one skilled in the art. For the production of coating media, the usual industrial lacquer additives may optionally be added to the crosslinking and vehicle components which are used according to the invention. Examples of such additives include anti-crater agents, anti-foaming agents, flow media, anti-settling agents, viscosity regulators, UV stabilisers and bonding agents. The properties affecting application and film formation can be influenced by the amount of additives.

Known pigments and/or extenders may optionally also be incorporated in the coating media. The relevant methods, e.g. dispersion or milling, have frequently been described in the literature. The usual pigments for clear or covering lacquers are suitable as pigments, for example carbon black, titanium dioxide, finely dispersed silica, aluminium silicate, French chalk, organic and inorganic colorant pigments, transparent colorants, metallic pigments or crosslinked polymer microparticles. Primers, extenders, metallic lacquers, coloured covering lacquers or clear lacquers may be produced depending on the pigment selected.

In addition to water, the coating media according to the invention may contain non-reactive co-solvents. These serve to adjust the viscosity on application and to influence the flow behaviour, and also to achieve a given lacquer effect. Examples of such solvents include aromatic hydrocarbons, e.g. xylenes; aliphatic hydrocarbons, e.g. n-hexane or cyclohexane; ketones, such as acetone or methyl isopropyl ketone for example; esters, such as butyl acetate or ethyl acetate, for example; and ethers, such as methoxypropanol or butoxypropanol, for example. However, alcohols may also be used, such as isopropanol, hexanol or ethyl glycol, for example. The properties relating to application and flow behaviour can be influenced by the boiling point or the different dissolving powers of the solvents. The amount of

solvent added thus depends on the desired properties, particularly on the viscosity properties, of the coating medium. True solutions, emulsions or dispersions are formed when water is used as the solvent. Coating media which contain water have a particularly low content of volatile organic solvents.

The coating media produced from the vehicles according to the invention may be adjusted to the desired viscosity for application by correspondingly regulating the addition of water and/or additives.

Depending on the quantitative proportion of component 1 to component 2, on the equivalent weight and on the amount of catalyst, the coating media can be adjusted to give a pot life between a few minutes and several hours.

The coating media produced in this manner may be applied in the usual way, for example by immersion, spraying, brushing or by an electrostatic route.

The coatings produced from the coating media may be hardened over a broad temperature range, from +5°C to 180°C, for example. The temperature range is preferably 20°C to 180°C, for example room temperature.

The coating media produced from the vehicles according to the invention are suitable for coatings which adhere to a multiplicity of substrates, such as wood, textiles, plastics, glass, ceramics, and metals in particular. The coating media may also be used in a multilayer process. For example, they may be applied to the usual primers, base lacquers or extenders, or to covering lacquers which already exist. The vehicles according to the invention are particularly suitable for base lacquer, covering lacquer and clear lacquer compositions.

One preferred embodiment comprises the application of the coating medium according to the invention as a clear lacquer overcoat on to an aqueous base lacquer according to the invention. In this connection, a wet-in-wet procedure may be employed, or the base lacquer may be previously dried by heating. This results in the bonding of both layers being particularly good.

A particularly preferred area of application for the vehicles according to the invention is the preparation of coating media for coatings in the motor vehicle industry. The favourable hardening conditions of the coating media produced from the vehicles according to the invention make them particularly suitable for motor vehicle repair coatings also.

Accordingly, the present invention also relates to a process for the production of coatings on various substrates, in which a coating medium produced from the vehicle according to the invention is applied, and then dried and hardened. The present invention also relates to the use of the vehicle compositions according to the invention in primers, base lacquers, covering lacquers and clear lacquers.

The following examples serve to explain the invention. All parts (pts.) and percentages (%) are given by weight.

Example 1

Preparation of acetoacetic ester-functionalised component 1:

670 pts. trimethylolpropane and 1950 pts. acetoacetic ester were placed in a 4 litre three-necked flask fitted with a stirrer, reflux condenser, thermometer and dropping funnel. The mixture was heated with stirring until ethanol was split off. After 4 hours, 488 g distillate was obtained; the temperature was 175°C. A vacuum was applied and the distillation was continued until a total of 806 g distillate

was obtained. The acetoacetic ester-functional component 1 produced then had a theoretical solids content of 96.5 %, a viscosity of 172 mPas and an acid number of 131.6 mg KOH/g solid resin.

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In the following, trimethylolpropane triacrylate (TMPTA) was used as the polyacryloyl compound.

Example 2

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Preparation of an aqueous emulsion from components 1 and 2 (emulsion 3).

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155.2 g of a 10 % aqueous solution of an emulsifying agent based on a polyoxypropylene polyoxyethylene sorbitanic acid diester were placed in a 1 litre flask at 60°C. The mixture was stirred using a stirrer rotating at a speed of about 7500 revolutions per minute. A mixture of 198.3 pts. of the acetoacetic ester-functionalised component 1 and 151.7 pts. TMPTA was added at 60°C over three minutes. 50 g demineralised water were added. The milky-white emulsion obtained had a solids content of 66.1 %.

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Example 3

Preparation of an aqueous base lacquer:

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a) 100 pts. of the aqueous emulsion 3) were homogenised with 23.61 pts. demineralised water and 24.9 pts. of a commercially available 3 % thickener paste (rheological additive) with intensive stirring.

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b) 4.77 pts. of a 65 % solution of a commercially available aluminium paste in white spirit/demineralised water (17.5 %/17.5 %), 3.74 pts. butyl glycol, 0.35 pts. of a commercially available corrosion inhibitor to prevent gassing of the aluminium, 0.7 pts. N-methyl pyrrolidone

and 2.34 pts. butanol were mixed separately. The mixture was adjusted to a spraying viscosity of 20'' using demineralised water.

5 Example 4

Preparation of an aqueous clear lacquer:

- 10 a) 49.1 pts. of the aqueous emulsion 3) were mixed with 10 pts. of a commercially available thickener and 40.9 pts. demineralised water, and then homogenised with 100 pts. of a 10 % solution of DBU in demineralised water, followed by adjusting to a spraying viscosity of 20''.

15 Example 5

20 The base lacquer from Example 3 was applied by spraying to a metal sheet provided with a commercially available two-component polyurethane extender, aerated for 35 minutes at room temperature, and the clear lacquer from Example 4 was then applied. The sample was aerated again for 40 minutes and then stoved at 60°C for 45 minutes.

25 The film obtained had a good hardness, exhibited good flop and good body and gloss.

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